

Kevlar 49 fibres: Thermal expansion coefficients from high temperature

X-ray data

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Axial and basal plane coefficients of thermal expansion have been estimated for Kevlar 49 fibres using high temperature X-ray diffraction data. The monoclinic unit cell exhibits an anisotropy behaviour. Whereas the axial dimension contracts with heating, the basal plane expands. The unit cell, however, registers an overall increase in volume.

SUCCESSFUL use of high temperature engineering materials demands an accurate and detailed prior knowledge of their properties and behaviour at elevated temperatures. Among the various thermal characteristics, the coefficient of thermal expansion (CTE, α) is an important parameter. Kevlar fibres, on account of their low density, high tensile strength and modulus, have a wide range of applications. These fibres are recommended for use up to 250–300°C (refs 1, 2).

Enlargement of dimensions is indeed the commonly expected effect of heating on most materials. Kevlar fibres behave differently: they manifest a negative axial CTE and a positive coefficient in the transverse plane. Negative axial CTE though not very common is not unique to Kevlar. PE³, carbon⁴, PBO⁵, Technora⁵, hinged polydiacetylene⁶ and some composites⁷ are examples of polymers which exhibit a negative axial thermal expansion. Non-polymeric materials such as Si (ref. 8), invar⁹, super invar⁹, powdered D₂O and H₂O (ref. 10), synthetic diamond¹¹, glasses¹², etc. also are characterized by negative CTEs. The temperature over which the CTE is negative varies with the material.

In the case of Kevlar, the negative axial CTE is closely associated with its structural characteristics. Molecules of PPTA (I) of which Kevlar is made¹³ include inherently planar phenyl groups and amide segments. In the monoclinic crystal structure of Kevlar, derived independently by both Northolt¹⁴ and Tashiro *et al.*¹⁵, the PPTA chains assume a fully extended all-*trans* conformation (Figure 1). Thus the chemical as well as the crystallographic structural characteristics endow the PPTA chains with a rigid rod-like character. Such rod-like molecules are arranged in layers which coincide with the crystallographic *bc* planes. The layer structure is stabilized, primarily, by interchain hydrogen bonds. On account of the periodic network-like arrangement of the hydrogen bonds (Figure 1), the layer itself acquires a fair amount of rigidity. It

appears therefore that the fully extended all-*trans* molecular conformation of the rigid molecule and their arrangement in layers, are factors which inhibit axial expansion of the PPTA chains during heating. In the crystal structure of Kevlar, the PPTA chains are oriented nearly parallel to the crystallographic *c* axis which is also the unique axis of the monoclinic unit cell. Thus, the *c* length of the unit cell represents the axial dimension of a monomer which, as mentioned earlier, is in a fully extended all-*trans* conformation. A negative axial CTE implies reduction in this axial dimension.

Despite the extensive use of Kevlar fibres in structural engineering, studies on the estimation of its CTE have not been many. Anisotropy in the thermal expansion behaviour of Kevlar 49 fibres was first reported by DuPont Inc., USA¹⁶, which commercially introduced these fibres. Later, Strife and Prewo¹⁷ measured the CTE of uni- and bi-directionally reinforced Kevlar composites, using dilatometry. In both the cases, the thermal expansion of the composite was shown to be anisotropic. They also employed theoretical models to predict the thermal expansion behaviour. The work of Rojstaczer *et al.*¹⁸ concerns estimation of the linear coefficient of thermal expansion of both Kevlar fibres and unidirectional Kevlar composites, using a thermo-mechanical analyser. They showed that the axial CTE of the fibre was more negative than what was reported by DuPont. Their values are -5.7 and $-6.3 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for the temperature ranges 20 to 80°C and 100 to 150°C, respectively. The value reported by DuPont is $-2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

It must be pointed out that the presently available data on the CTE of Kevlar fibres or Kevlar reinforced com-

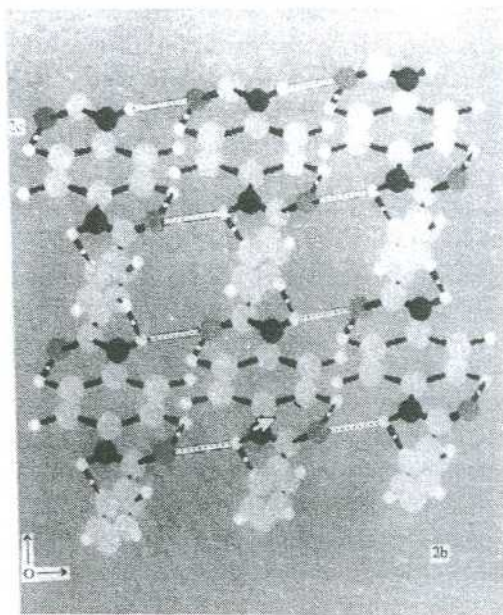


Figure 1. The arrangement of PPTA molecules in the crystal structure. Dashed lines (---) represent interchain hydrogen bonds. Intramolecular steric interactions relevant to the orientation of the phenyl rings have been indicated as bonds with central dots.

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posites are all based on either macro measurements or are theoretically estimated. To date, crystallographic data on the thermal expansion behaviour of Kevlar 49 fibres are not available. Previous studies conducted by Hindeleh and Abdo¹⁹ and Iyer and Vijayan²⁰ have independently reported the high temperature X-ray data on Kevlar 49 fibres. Hindeleh and Abdo have described the effect of annealing for ≈ 10 min on the crystallinity and microparacrystallite dimensions of Kevlar 49 fibres. Iyer and Vijayan's study provided similar data on the effect of prolonged thermal ageing on the crystal structural characteristics. Their X-ray results, however, pertain to the basal plane features and information concerning the axial characteristics have not been included. Both these investigations do not concern the CTE of the fibre. In this communication, we report the first X-ray analysis of the effect of *in situ* heating on the crystallographic unit cell dimensions of Kevlar 49 fibres. The dimensional changes have been used to estimate the corresponding CTEs.

A bundle of Kevlar 49 fibres ~ 0.3 mm thick were held taut in the high temperature attachment for fibres supplied by M/s Rigaku International Corporation, Japan for the D/MAX 2200 Ultima X-ray powder diffractometer. Individual equatorial and meridional patterns were recorded in the 2θ ranges 10–55 and 9–45°, respectively, using $\text{CuK}\alpha$ radiation. The patterns were recorded at room temperature (RT $\approx 20^\circ\text{C}$), 50, 100, 150, 200, 250 and 280°C, respectively. The heater assembly supplied by Rigaku consisted of a semi cylindrical metal foil surrounding the tautly held fibre sample. A chromel–alumel thermocouple was used to measure the temperature (T) of the sample. At each of the chosen temperatures, heating was carried out at an approximate rate of $5^\circ\text{C}/\text{min}$. After reaching the desired temperature, a minimum of 10 min was allowed for stabilization. During the recording of the diffraction patterns, the temperature was found to remain stable up to $\pm 0.5^\circ\text{C}$. It must be mentioned that the presence of the heater assembly on the fibre sample holder necessitated recording of the patterns in the ϑ_{fixed} mode. All the patterns were recorded with $\vartheta_{\text{fixed}} = 8^\circ$.

The 2θ range selected for the equatorial pattern included the two most intense reflections from Kevlar fibres, viz. (200) and (110). These reflections exhibit a slight overlap in the tail region the effect of which was removed using the peak separation software package supplied by Rigaku. The meridional patterns included three (00l) reflections, viz. (002), (004) and (006). Of these, the low angle reflection (002) included the effect of proximity to the direct beam and hence could not be used reliably for further analysis. In the case of the higher angle reflection (006), the choice of the ϑ_{fixed} geometry led to the introduction of an arbitrary asymmetry in the shape of the profiles. Further details of this geometric effect will be reported elsewhere. However, the consequent effect was that the reflection (006) could not also be used reliably. On account of these limitations, in the subsequent analysis

of meridional data information from only the (004) reflection was used.

The profile characteristics were derived by least squares fitting of a pseudo Voigt function. The basal plane dimensions of the unit cell were derived from the equatorial reflections (200) and (110) and the axial length c from the meridional reflection (004). From considerations of standard deviations of the parameters, use of three reflections to derive three unit cell parameters may appear rather meagre. However, the number is just sufficient to evaluate the unit cell constants. As is well known, the number of observed reflections in fibre diffraction patterns, is invariably far less than in the patterns from single crystals. Also, the number of reflections which are sufficiently intense and consequently reliable for use in further detailed analysis, is often very small. On account of these limitations, structural information on fibrous polymers is often based on scanty X-ray data.

The high temperature X-ray diffraction patterns from Kevlar 49 fibres resemble the room temperature pattern, thereby showing that the initial monoclinic crystal structure was retained at high temperatures also. Figure 2 presents the composite, equatorial and meridional profiles, respectively. Thermally induced shifts in the 2θ values, though very slight can be clearly appreciated from these overlapped profiles.

As could be expected from a polymer with negative axial CTE, the c axial length of the unit cell reduces with

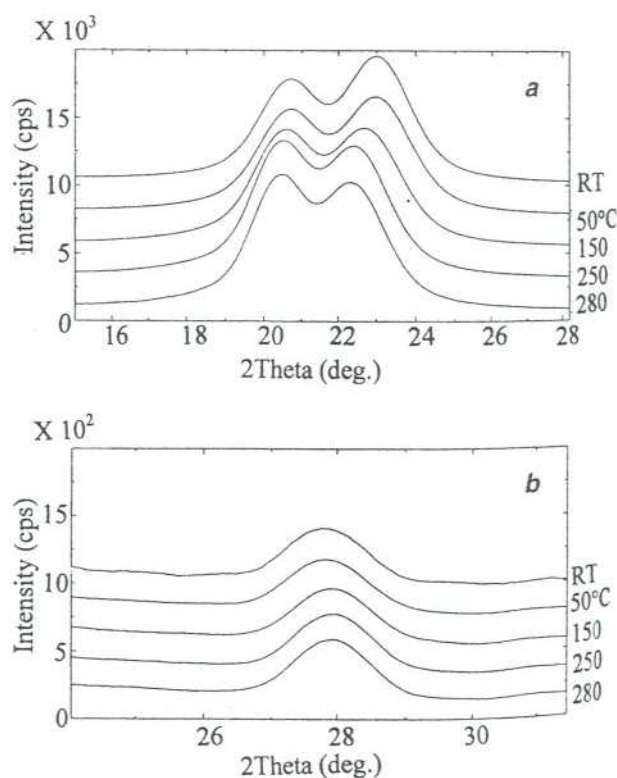


Figure 2. Composite diffraction profiles. *a*, Equatorial (110) $2\theta \sim 20.7^\circ$ and (200) at $\sim 22.9^\circ$; *b*, Meridional (004).

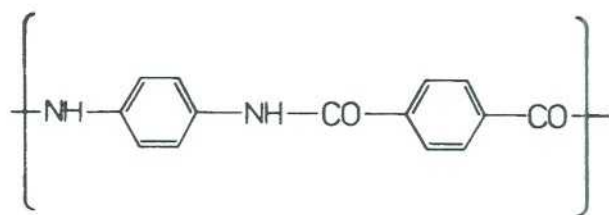
increase in T . Figure 3 depicts the observed variation. Up to 150°C, the linear reduction in c is fast, beyond which temperature, the reducing trend continues albeit at a slower pace. Values of CTE estimated from adjacent c values (Figure 3) also reflect this feature. The magnitudes of α_c obtained from the present X-ray analysis are conspicuously higher than those reported by Rojstaczer *et al.*¹⁸. It must be pointed out that the X-ray values represent the behaviour of the crystalline fraction of the fibre whereas Rojstaczer *et al.*'s macro measurements represent the entire fibre. The observed difference between the two sets of data suggests that in moving from the crystallographic unit cell to the macro fibre, appreciable damping of the α_c values has occurred. Rojstaczer *et al.*'s data include the effect of heating on the crystalline lattice as well as other physical factors such as impurities, interface between crystallites, etc. which characterize the fibre. The response of these additional physical factors to heating can be different from that of an ordered crystal lattice and thus lead to differences between the α_c values estimated by the X-ray and other macro methods.

Having established the axial contraction of the unit cell, the question to be addressed was concerning the possible correlation between the contraction and the structural feature. If the rigidity of the PPTA molecule inhibits axial expansion, how does it permit contraction? In the case of PPTA, reduction in axial dimension by chain folding is not favoured because of the molecular rigidity. The following types of structural deformations may, however, be considered to explain the introduction of axial contraction.

Let us consider partial changes in molecular conformation. The observed reduction in c value can be accounted for, at least partially, on the basis of thermally induced

conformational disorders, viz. introduction of partial changes from the initial all-*trans* conformation. It may be pointed out that similar conformational disorders have been proposed to account for the changes in axial dimensions of PTFE²¹ at elevated temperatures. The question to be addressed is what triggers such conformational changes? Could there be a build up of localized, internal strain which in turn, lead to conformational changes?

Slight changes in molecular dimensions can also account for the negative CTE. In the case of polyethylene (PE) which also has a negative axial CTE and an initial, fully extended all-*trans* molecular conformation like Kevlar, the concept of rotations about C-C single bonds has been used³ to account for the negative axial CTE. As seen from structure (I), in the case of the PPTA molecule,



(I)

Structure I.

such single bonds do not exist. The molecular characteristic which appears viable for change is the orientation of the phenyl rings. In the crystal structure reported by Northolt¹⁴, the angle of tilt between the phenyl group of the terephthalic segment and the adjacent amide bond is $\sim 30^\circ$ and in the *p*-phenylene diamine segment, the phenyl group is tilted with respect to the adjacent amide plane by $\sim 35^\circ$. These orientations are controlled primarily, by intra-molecular steric interactions as shown in Figure 1. The tilts of both the phenyl rings appear to be delicately controlled by short contacts on either side. Any deviation from this initial orientation would only tend to increase the steric repulsion on one side or the other of the phenyl rings. Therefore it appears that if the tilts of the phenyl rings get altered during the process of heating, the resulting arrangement is likely to represent a sterically less favourable or a strained state of the molecule. Introduction of such strains may be correlated with the conformational changes of the type described in the previous section, which in turn lead to axial contraction. However, the above-mentioned correlation between axial contraction and structural changes are only predictive in nature.

Figure 4a depicts the percentage variations in the a and b lengths of the unit cell. The corresponding variation in the basal plane area $A (= ab)$ is presented in Figure 4b. In contrast to the axial length, the basal plane area exhibits a progressive enhancement with T , the fractional increase being $\sim 4\%$ at 280°C. The increase in the basal plane area

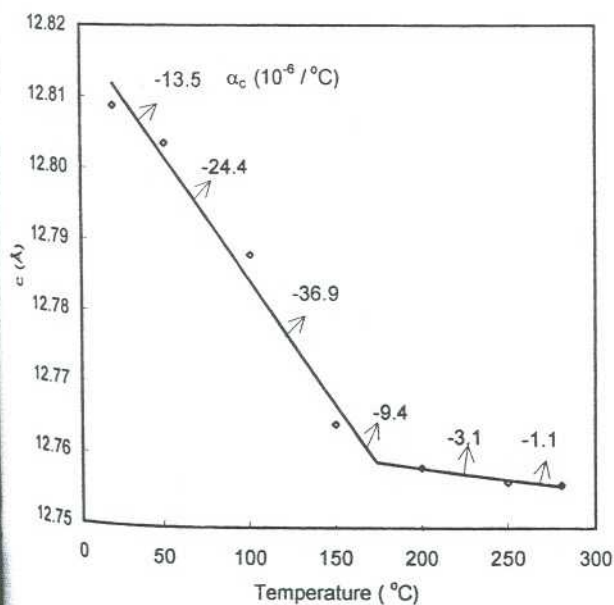


Figure 3. Variation of the c axial length with T . α_c values corresponding to adjacent data points have been marked.

is primarily due to increase in the a value which is $\sim 3\%$ at 280°C . Changes in the b dimension are comparatively less. The preferential increase in the a value is understandable because in the crystal structure of Kevlar, the crystallographic a direction represents a concentration of weak, van der Waal's interactions existing between adjacent layers. Any type of deformation, thermal or otherwise, may hence be expected to influence readily the already weak interactions. The b dimension, on the other hand, represents the distance between adjacent chains linked by hydrogen bonds. Earlier studies²⁰ on thermally aged Kevlar fibres have shown that the PPTA chains have

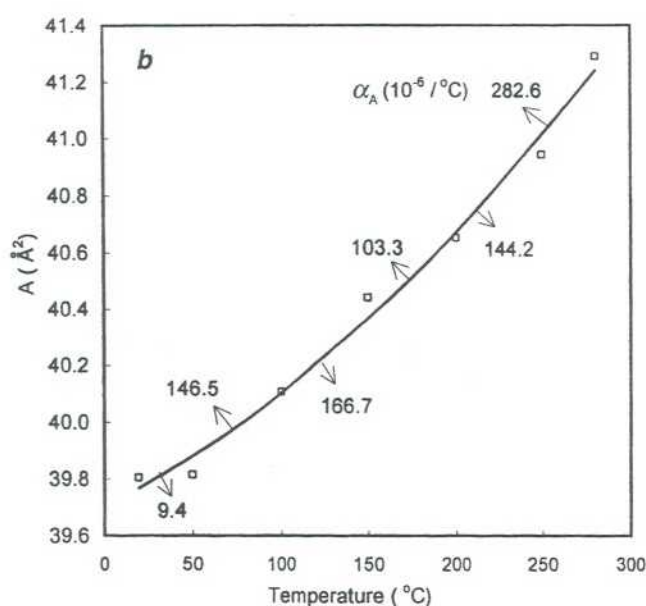
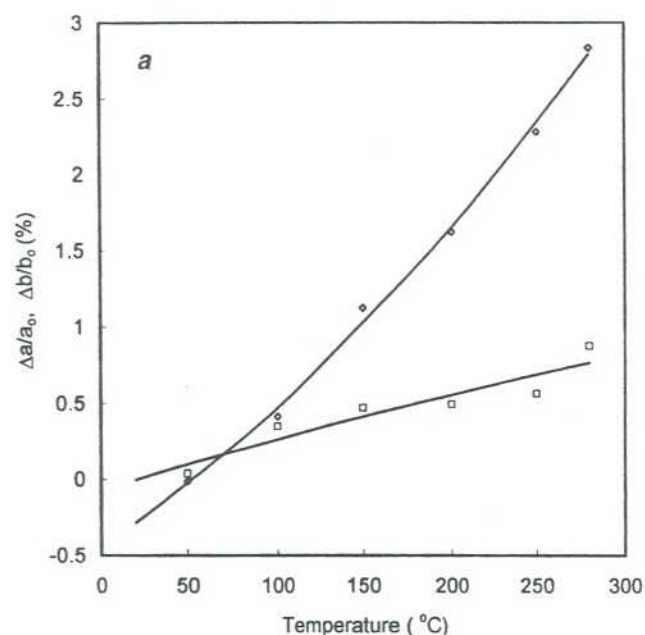


Figure 4. *a*, Thermally induced variations in the basal plane dimensions. $\circ \Delta a/a_0 \times 100$; $\square \Delta b/b_0 \times 100$; *b*, Variation in the basal plane area with T . Values of α_A corresponding to adjacent data points have been marked.

a propensity to retain the interchain hydrogen bonds even after prolonged thermal exposures. Consequently, the b length of the unit cell was also found to stay fairly uninfluenced by the thermal history of the sample. The present study provides further evidence for such a behaviour.

Figure 4 *b* also presents the thermal expansion coefficients, α_A calculated using adjacent data points. The value of $66.3 \times 10^{-6}^\circ\text{C}^{-1}$ reported by Rojstaczer *et al.* matches with the interpolated value for α_A in the temperature range 50 – 100°C of the present data set. These observations indicate that in the axial direction as well as in the perpendicular basal plane, a qualitative agreement exists between the CTE values measured by X-ray and macro methods.

In Figure 5 variations of CTEs calculated with respect to the initial values of dimensions, viz. c_0 and A_0 respectively with T are recorded. The conspicuous feature is the two-stage behaviour of both the parameters. Up to 150°C , both α_A and α_c exhibit a rapid change beyond which temperature α_A nearly stabilizes whereas α_c registers a continued reduction. The inset in Figure 5 has been included to emphasize on the dip in the α_c value observed at 150°C . It may be pointed out that at this point of inflexion, the c value does not start increasing. The dip only represents continuation of contraction occurring, however, at a comparatively slower pace.

The two-stage behaviour seen in Figure 5 thus demonstrates that the influence of heating on the unit cell dimensions is not the same all along the heating process. At 150°C a distinct change occurs. Interestingly, this change is common to both the axial direction and the basal plane. At the present moment, it is not clear what exactly causes the two-stage behaviour. Earlier studies²⁰

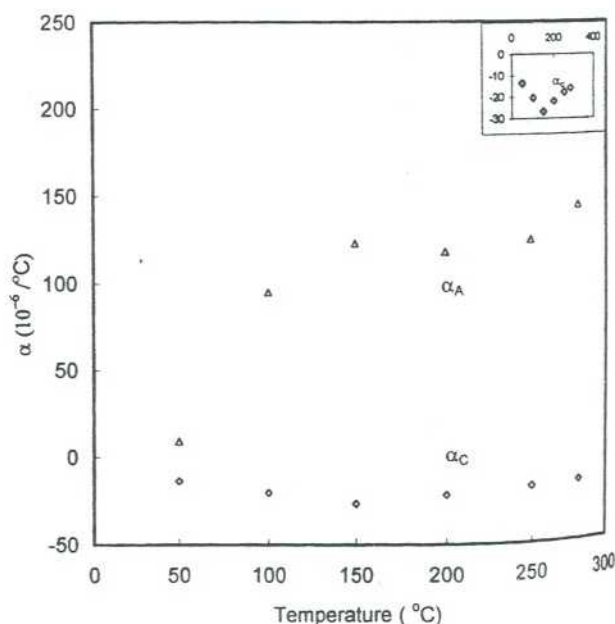


Figure 5. α values calculated with respect to initial dimensions vs T . Inset shows the dip in α_c at 150°C .

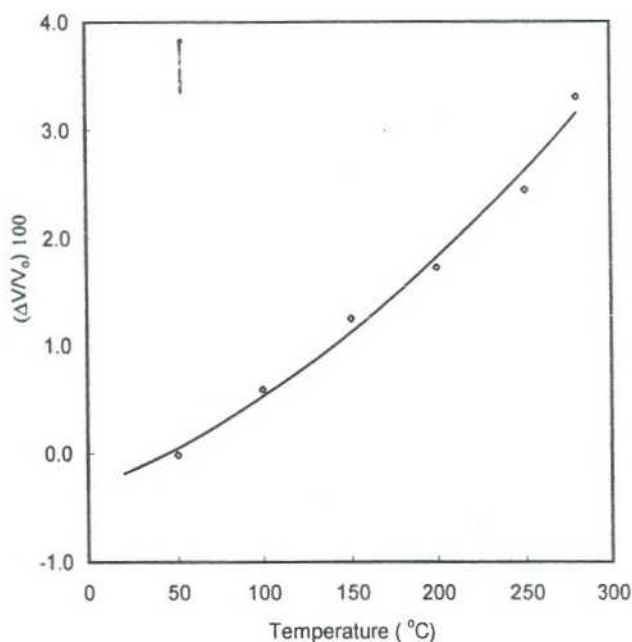


Figure 6. Percentage variation in the unit cell volume with temperature.

on the effect of prolonged thermal ageing of Kevlar fibres have indicated the onset of several thermally induced structural deformations. It is not unlikely that similar thermally induced deformations which get initiated at 150°C are responsible for the two-stage behaviour seen in Figure 5. For separating the thermally induced expansion/contraction from the possible effects of any other structural deformation, it is necessary to conduct further detailed experiments.

Figure 6 depicts the percentage variation in the unit cell volume with temperature. Despite the reduction in the c length, the unit cell registers an overall increase in volume. Such an increase is due to difference in the magnitudes by which the basal plane expands and the axial length contracts. The former is always more than the latter. As seen in Figure 6, at 280°C the unit cell expands by 3.3%.

Dimensional instability arising from the negative CTE of Kevlar fibres and the positive CTE of a matrix has often been a cause of concern to users of Kevlar composites at elevated temperatures. It must be emphasized here that such a dimensional instability is serious primarily in unidirectional Kevlar composites. As indicated by both X-ray and macro measurements, despite the axial contraction, the entire fibre undergoes an overall volume expansion during heating. Hence, in composites which are not unidirectional, both the fibre and the matrix should manifest expansion in volume although their magnitudes may differ.

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